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A Direct, Continuous, Low-Power Catalytic Conversion of Methane to Higher Hydrocarbons via Microwave Plasmas

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A selective, direct, continuous, low-power catalytic conversion of methane to higher energy hydrocarbons via microwave plasma methods has been developed in the pressure range 10 to 50 Torr. Methane can be converted to ethane, ethylene, and acetylene in different selectivities depending on the power of the plasma, flow rate, nature of the catalyst, and pressure in the system. Selectivities for ethane can be as high as 77%, for ethylene 25%, and for acetylene 25%. Conversions of methane as high as 52% have been realized. Coking can be minimized by proper choice of catalyst and high flow rates. Ethane and ethylene can be converted with 100% selectivity to ethylene and acetylene, respectively, in a similar process. Radicals are important in these transformations, with the catalyst surface providing sites for radical combination. Rates of reaction, energy balances, and mechanisms of reaction are discussed. © 1993 Academic Press, Inc.

1. INTRODUCTION

Selective activation of carbon hydrogen bonds has been the goal of researchers in hetereogeneous (*1*) and homogeneous (*2*) catalysis for over 50 years. Selective activation of saturated hydrocarbons like methane and ethane is difficult due to the similar high dissociation energy of activation of most C–H bonds in these and similar molecules.

Various activated C–H bond species have been isolated as intermediates in metal clusters (*3*), and diffraction studies have shown that selective activation can be achieved in model complexes. It has often proven to be more difficult to selectively activate hydrocarbons to form higher hydrocarbons (*4*), although this area has been a subject of great interest in the last 10 years.

Significant advances in heterogeneous catalytic conversion of methane have been made in recent years by several groups including Lunsford (*5*), Klier (*6*), Keller and Bhasin (*9*), and others (*7*). These researchers have found that metal and mixed metal oxides can be heated to temperatures between 300 and about 800°C in order to produce oxygenated high energy hydrocarbon products from methane such as methanol, formaldehyde, ethane, ethylene, and others. Three main mechanisms have been suggested, including steam reforming, partial oxidation, and oxidative coupling. Recently, strong evidence has been obtained that gas-phase radicals may be important in oxidative coupling reactions (*8*).

Coupling reactions are of considerable interest here. Researchers at Union Carbide Corporation (*9*) have produced coupled products of ethylene and ethane from methane at elevated temperatures over various oxides. High selectivity can be attained, although low activities are commonly reported under these conditions. Total oxidation products such as CO_2 and CO are observed in these reactions.

A plasma can be defined as an electrically conducting gas. Gas-phase species include ions, electrons, and ground state and ex-

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cited state species. The use of plasmas for chemical purposes has been limited to diamond coatings (*10*), preparation of ceramics (*11*), and conversion of specialty chemicals like radiopharmaceuticals (*12*). The combination of plasmas and catalysts (*13*, *14*) is also relatively unexplored. DC arc plasmas have been used to produce C_2H_2, NH_3, and N_2O without a catalyst (*13*). Early research with glow discharge plasmas suggested that total oxidation of hydrocarbons to CO and CO_2 occurred and that electrodes were eventually coated by hydrocarbons and rendered inactive (*13*). On the other hand, radical formation in plasmas has been known for quite some time (*15*).

The production of ethylene and ethane from methane that has been activated in a microwave plasma is the subject of this paper. This plasma system involves a low-power, low-temperature plasma operated at less than 100 W (*16*). Methane is flowed through a quartz reactor into the plasma zone with or without a catalyst downstream from the plasma. Products are detected by chromatographic methods.

Selectivities and conversions are reported as the pressure, flow rate, and plasma power are varied. Side products such as polymeric deposits are also dependent on these three variables.

II. EXPERIMENTAL SECTION

Methane, ethane, ethylene, acetylene, argon, and other gases were obtained from Matheson and used without further purification. A copper tubing manifold was assembled with flow meters, shutoff valves, needle valves, and mixing valves so that reactant gases could be mixed or fed separately into the plasma reactor. Bubble meters were also used to measure flow rates before and after the reactor.

The copper tubing was connected to the quartz plasma reactor tube via Cajon fittings purchased from Hartford Valve and Fitting, Hartford, CT. Two separate gas inlets were fed into a Y-shaped quartz plasma reactor having an outside diameter of 12 mm and and an inside diameter of 10 mm. The outlet of the Y-tube had a depression in it for holding catalyst about 2 in downstream from the center of the Y. Right after the center of the Y-tube was a 1/4-wave Evenson cavity that was connected to a Raytheon Microwave generator which had a meter for measuring forward and reflected power.

The plasma was initiated with either a Tesla coil or a static gun while Ar flowed through the reactor, which had a volume of about 5 ml. The area of the plasma was maximized with a coupler (tuning stub) on the cavity under flowing Ar and then the feed was switched to pure hydrocarbon.

Vacuum pumps were attached to the reactor to provide vacuum to control the plasma. Products were analyzed on stream as well as by trapping volatile species in liquid nitrogen and expanding these into a bulb of known volume. A diagram of the system which has an overall volume of about 173 ml is given in Fig. 1. Catalysts were placed downstream of the reactor right at the edge of the plasma zone. The exit of the reactor was often at a smaller diameter, which was believed to cause turbulent flow and better mixing than with a tube of the same diameter throughout.

Product analyses were done with an HP 5880A gas chromatograph. A Porapack Q-S and a Porapack Q-T column were connected in series for separation of products. An oven temperature of 100°C, and injection temperature of 200°C, and a detector temperature of 225°C were used. A thermal conductivity detector was used with He carrier gas.

About 0.3 g of catalyst was used for all experiments dealing with use of catalysts. The Ni catalyst was a commercial material from Harshaw (Ni-0302 T1/8) in the form of pellets.

III. RESULTS

A summary of experiments including catalysts, pressure of reaction, power supplied by the microwave generator, flow rate, conversion, and selectivity is given in Table 1.

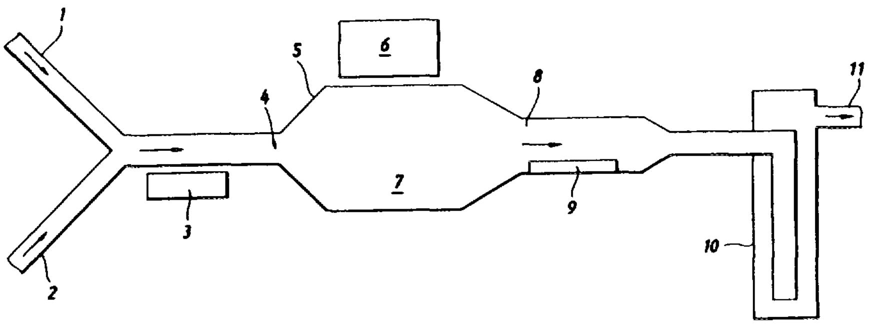

FIG. 1. Microwave plasma reactor: (1) inlet, (2) inlet, (3) pretreating zone, (4) inlet orifice, (5) quartz reactor, (6) Evenson 1/4-wave cavity, (7) plasma zone, (8) outlet orifice, (9) catalyst, (10) trap, and (11) outlet to hood or gas chromatograph.

Experiments were done with and without catalyst and with either methane, ethane, ethylene or a 50/50 mixture of methane and ethane. Data from Table 1 are referred to as Ex. 1 for the entry under #1.

In general, ethane is selectively (100%) converted to ethylene (Ex. 10, 11), ethylene is selectively (100%) converted to acetylene (Ex. 15), and methane is converted to ethane, ethylene (Ex. 12–14), and under certain conditions acetylene (Ex. 6–9). As flow rate is increased from 50 to 500 ml/min, production of acetylene is eliminated.

Conversion of methane ranged from 4% (Ex. 12–13) to 38% (Ex. 8). Conversion was maximized at 60 W (Ex. 8), an intermediate value of the power supplied by the generator, as shown in Fig. 2. Selectivity to ethylene was also maximized (25%) near 60 W (Ex. 8), as shown in Figure 3.

Most work with catalysts was done at 80-W power supplied by the generator (Ex. 4–5, 16–17). Catalysts were placed in the quartz reactor tube beyond the microwave cavity in all cases. A gauze of Pt or Ni powder were used as catalysts. Conversion stayed at 31% without any catalyst (Ex. 7) with respect to Ni catalyst (Ex. 4) at 50 ml/min flow rate of methane, whereas selectivity to acetylene decreased. Extending the time of plasma treatment from 20 to 40 min (Ex. 5) increased the selectivity to acetylene somewhat without loss in conversion.

Experiments done at 60 W in the presence of Ni catalyst showed a conversion of 52% with similar selectivities as without catalyst, 25% ethylene, 25% acetylene, and 50% ethane.

At a flow rate of 500 ml/min Ni catalyst (Ex. 17) had a conversion of 8% with respect to 4% without any catalyst (Ex. 12) and similar selectivities toward ethane (~25%) and ethylene (~75%). Pt gauze catalyst (Ex. 16) had a lower conversion of 6% with similar selectivities.

Polymeric deposits generally were produced when the flow rate was 50 ml/min and minimized at high flow rate (500 ml/min). Mixtures of methane and ethane used as feed (Ex. 1, 2) led to products of ethane, ethylene, and acetylene with conversions less than that of methane or ethane alone.

Coke formation was apparent in experiments 4, 5, 7, 9, 15, and 18 as evidenced by formation of polymeric deposits. Experiment 8 did not yield any coke as detected visually, and mass balance data indicate less than 1% coke for this reaction.

IV. DISCUSSION

Interpretation of the microwave plasma results of Table 1 and Figs. 2 and 3 is generalized below with respect to selectivity, conversion, energy balance, rate of reaction and, finally, comparison to other plasma and microwave results in the literature.

TABLE 1

Summary of Microwave Plasma Reactions

#	Feed	Catalyst	P	Power	Flow	Conv.	Select
1	C1/C2	None	27	80	200	4	[a]
2	C1/C2	None	23	80	100	6	[a]
3	C1	Ni	50	80	500	8	$C2^=$, 23.5 C2, 76.5
4	C1	Ni	10	80	50	31	$C2^=$, 19.1 acetylene, 33.7 C2, 47.2
5	C1	Ni	10	80	50	31	$C2^=$, 21.3 acetylene, 37 C2, 41.7 long reaction time
6	C1	None	23	80	100	26	$C2^=$, 25.3 acetylene, 24 C2, 50.7
7	C1	None	10	80	50	31	$C2^=$, 20.6 acetylene, 38.4 C2, 40
8	C1	None	10	60	50	38	$C2^=$, 25 acetylene, 25 C2, 50
9	C1	None	10	40	50	31	$C2^=$, 23.1 acetylene, 23.8 C2, 53.1
10	C2	None	23	80	100	7	$C2^=$, 100
11	C2	None	20	80	50	10	$C2^=$, 100
12	C1	None	40	80	500	4	$C2^=$, 24.9 C2, 75.1
13	C1	None	40	60	500	4	$C2^=$, 22.8 $C2^=$ 77.2
14	C1	None	50	40	500	3	$C2^=$, 25.1 C2, 74.9
15	$C2^=$	None	23	80	100	41	acetylene 100
16	C1	Pt	50	80	500	6	23.5 $C2^=$ 76.5 C2
17	C1	Ni	50	80	500	8	27 $C2^=$ long reaction time
18	C2	None	20	40	50	4	100 $C2^=$
19	C1	Ni	10	60	50	52	$C2^=$, 25 acetylene, 25 C2, 50

Note. P in Torr; power in watts, power supplied by generator; flow in ml/min; conv. in %; selectivity in %; C1 = methane, CH_4; C2 = ethane, C_2H_6; $C2^=$ = ethylene, C_2H_4; time of experiments, 20 min; long reaction time, 40 min.

[a] Not determined.

A. Selectivity

Methane can be continuously activated in a microwave plasma to produce ethane, ethylene and acetylene. Ethane is selectively converted to ethylene, whereas ethylene is selectively converted to acetylene, as shown in Table 1. Selectivity is influenced

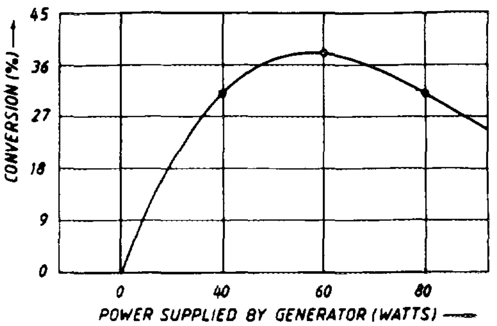

FIG. 2. Plot of % conversion vs power supplied by generator (in watts).

by power, flow rate, and the presence of catalyst. The observation of maximum selectivity at an intermediate power level, as shown in Fig. 3, is in contrast to previous research (*17*) at much higher power levels (500–2000 W). This enhanced selectivity is likely due to the efficiency (*vide infra*) of the microwave apparatus used in experiments reported here, as well as minimization of coke formation.

Coke formation is minimized by either increasing the flow rate above 50 ml/min in these experiments or by using incident power levels of less than 80 W. These observations are in contrast to those of Kawahara, where coke formation was always observed at the higher power levels used in such experiments (*17*).

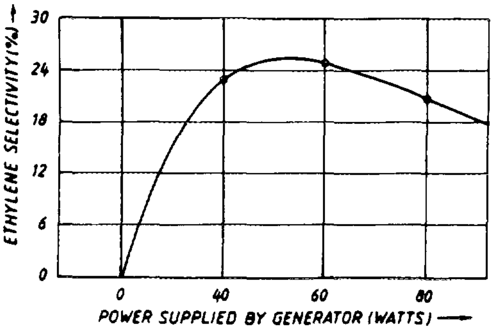

FIG. 3. Plot of ethylene selectivity (in %) vs power supplied by generator (in watts).

B. Conversion

The % conversion of methane is maximized at an intermediate power level (60 W), as shown in Fig. 2. This result was not obtained by Kawahara (*17*) at much higher power levels (500–2000 W) when a tapered waveguide cavity was used. In fact, the relationship of Wiener and Burton (*18*) used to estimate conversion (*17*) from power level does not hold under our conditions using a resonance cavity.

Conversion was maximized in our experiments by initially starting the plasma with Ar and adjusting the tuning stub to maximize the area of the plasma followed by a gradual switch to hydrocarbon feed. Initial experiments with the catalyst in the microwave cavity led to considerable coke formation on the catalyst and on the walls of the reactor, leading to subsequent experiments with the catalyst downstream of the plasma zone (see Fig. 1). Conversion is also related to overall pressure, power, flow rate, and other factors discussed below.

C. Energy Balance

The energy requirements for the conversion of methane have been experimentally determined based on example 8. A balanced chemical equation for this example is given below:

$$CH_4 \rightarrow 0.25\,C_2H_6 + 0.125\,C_2H_4 + 0.125\,C_2H_2 + 0.875\,H_2. \quad (1)$$

The enthalpy (ΔH) for this reaction is 21.166 kcal/mol of CH_4. The reaction is endothermic and requires an input of energy in order to proceed.

For a 50 ml/min flow rate, 60 W supplied by the microwave generator, and a molar flow rate of 22.4 liter/mol, 3.294 J/sec or 3.294 W are needed to drive this reaction at 100% conversion. Two conclusions are apparent from this calculation. First the efficiency of the experiment is not great (3.294 W/60 W = 5.5%) and the reaction is a low-power process. A reviewer has pointed out that the calculated 3.294 W does not take into

TABLE 2

Determination of Reaction Rates

P (Torr)	Q (cc/sec)	Conversion (%)	V/Q (sec)	u (cm/sec)	Rate (sec^{-1})
10	50	0.38	1.81	1.66	0.223
20	100	0.17	0.91	3.32	0.188
50	500	0.04	0.18	16.6	0.221

Note. Q = flow rate; V = volume in cc; u = linear velocity; $u = Q/A$; residence = V/Q; rate = Q (% Conv.)/V.

account any energy barrier needed to activate methane. It is speculated here that the low efficiency of conversion is related to poor heat and light recovery and the difficulty in coupling microwave energy directly into the methane molecule. This is related to the type of cavity used in such experiments, which is optimized for ionization of rare gases rather than hydrocarbons. We are not aware of any cavities that have been specifically designed for hydrocarbons.

Finally, our experiments are considerably different as regards power consumption, power density, selectivity, and conversion than the high-power experiments of Kawahara (*17*), the pulsed microwave heating experiments of Wan (*19*), and the high-power experiments of McCarthy (*20*).

D. Rate of Reaction

Relative rates of reaction of methane conversion can be calculated from these experimental data. For a power of 60 W supplied by the generator the volume of the microwave plasma that was generated is 1.508 cc. The power density is 39.79 W/cc. A summary of various pressures (P), flow rates (Q), % conversion, volumes per flow rates (V/Q), linear velocities (u), and calculated rates of reaction for three different experimental runs is given in Table 2.

As pressure and flow rate increase, the reaction rate (Q(% conv.)/V) remains relatively constant. The specific type of reactor, therefore, is not an important variable because the reaction rate does not depend on the CH_4 concentration in the plasma zone. The shape of the reactor, therefore, such as a plug flow or continuously stirred tank reactor (CSTR), does not matter. The efficient transfer of microwave energy to reactants is a critical factor. Our data suggest that the power density of the reactor is a measure of the efficiency. Power density depends on microwave power, flow rate, and nature of the reactants. Flow rate is dependent in turn on pressure and overall dimensions (total volume) of the reactor.

Several questions arise concerning the surprising observation that reaction rate is independent of flow rate and residence time for the data of Table 2. It is likely (as suggested by a reviewer) that increased pressure coupled with lower flow rate may cancel each other. The volume of the reactor stays constant as flow rate is increased. It is also possible that an equilibrium is reached.

E. Microwave Plasma Activation of Hydrocarbons

Product selectivity is directly influenced by the flow rate, power, power density, and pressure of the reactor system. Our experimental data suggest that the major initial reaction is H-atom abstraction with concomitant formation of hydrocarbon radicals. For methane:

$$CH_4 \longrightarrow CH_3 + H \tag{2}$$

$$CH_3 \longrightarrow CH_2 + H \tag{3}$$

$$CH_2 \longrightarrow CH + H \tag{4}$$

$$CH \longrightarrow C + H \tag{5}$$

and

$$CH_4 \longrightarrow CH_2 + 2H \qquad (6)$$

$$CH_4 \longrightarrow CH + 3H \qquad (7)$$

$$CH_4 \longrightarrow C + 4H \qquad (8)$$

Reactions (2), (3), and (6) are desirable for the formation of ethane and ethylene from methane and are low-energy processes because they predominate at low power levels in these plasma reactions. Selectivity is optimized in the examples given here because reactions (4), (5), (7), and (8) have largely been minimized. Increasing the flow rate and decreasing power can suppress these undesirable reactions.

Radical recombination is perhaps responsible for product formation:

$$2CH_3 \longrightarrow C_2H_6 \qquad (9)$$

$$2CH_2 \longrightarrow C_2H_4 \qquad (10)$$

$$2CH \longrightarrow C_2H_2 \qquad (11)$$

By preventing formation of C, production of acetylene is achieved.

Feeds of methane and ethane support the generalizations of Eqs. (2)–(11). Data for ethane suggest that dehydrogenation to ethylene is the predominant reaction pathway:

$$C_2H_6 \longrightarrow C_2H_4 + 2H \qquad (12)$$

Activation of ethylene leads to selective production of acetylene, again via H abstraction:

$$C_2H_4 \longrightarrow C_2H_2 + 2H \qquad (13)$$

Another viable mechanism is that ethylene and acetylene are produced sequentially from methane, as in

$$CH_4 \longrightarrow C_2H_6 \longrightarrow C_2H_4 \rightarrow C_2H_2 \quad (14)$$

based on the fact that C_2H_6 and C_2H_4 yield C_2H_4 and C_2H_2, respectively as indicated in examples 10, 11, and 15 of Table 1.

Experimental data suggest that reaction (13) requires more energy than reaction (12). Since acetylene is formed from a methane feed, it may be possible that if ethylene species initially produced in the plasma reside too long then acetylene may be formed. This may explain why faster flow rates eliminate the formation of acetylene.

A comparison of operating conditions (pressures, residence times, incident power), % conversion, feedstocks, microwave mode, radiation, presence or absence of catalyst, % conversion, and yields for our data and those of Kawahara (*17*) Wan (*19*), and McCarthy (*20*) are given in Table 3. Longer residence times (*17*, *20*) do indeed lead to higher amounts of acetylene. The uniqueness of experiments reported here is related to low power density, continuous radiation, and use of catalysts.

Considerable research has recently been carried out with surface catalytic activation at elevated temperature (typically > 400°C) of methane over oxide catalysts such as Li/MgO, Sm_2O_3 and other materials (*5–9*). These catalysts are not active in plasma reactions reported here (same conversions and selectivities as with no catalyst), suggesting that different mechanisms are involved in these two different processes. The thermal temperature of our plasma reactor is considerably lower (<200°C) than these other systems, whereas the electronic temperature of the plasma is on the order of 2000 K. Catalysts in the surface catalytic activation systems (*5–9*) must activate C–H bonds and also serve as a surface for sorption and desorption. Catalysts in the plasma process primarily sorb H radicals produced in the plasma and act as surfaces for sorption of hydrocarbon radicals and desorption of products.

V. CONCLUSIONS

Methane can be activated via H abstraction by a direct, continuous, low-power-density microwave plasma process at low pressure in the range of 10–50 Torr. Selectivity toward ethylene and conversion can be enhanced via dehydrogenation catalysts like Ni. Feeds of ethane and ethylene can be selectively converted to ethylene and acetylene, respectively. Similar selectivity and conversion data have been obtained on

TABLE 3

Comparison to Other Microwave Processes

	This research		Kawahara (*17*)	Wan (*19*)	McCarthy (*20*)
Feedstock tested	CH_4 C_2H_6		CH_4 C_2H_6	CH_4	CH_4
Microwave mode	Plasma		Plasma	Heating	Plasma
Microwave radiation	Continuous		Continuous	Pulsed	Continuous
Catalyst	With/Without		Without	With	Without
Operating conditions					
Pressure (Torr)	High	100	40	760	380
	Low	10	10	760	[a]
Residence time (millisec)	High	25	10	60 sec/Batch	12 sec
	Low	10	1	20 sec/Batch	7
Incident power (watt)	High	80	2000	80	Up to 1500
	Low	40	500	80	[a]
Conversion %					
CH_4 feed (no carrier)	3 ~ 38		27 ~ 88	50 ~ 70	17 ~ 100
C_2H_6 feed	7 ~ 10		58 ~ 94		
Yields (*v*%, converted feed)					
CH_4 feed					
C_2H_2	0 ~ 24		45 ~ 89	0	34 ~ 95
C_2H_4	19 ~ 25		3 ~ 42	100	16 ~ 21
C_2H_6	40 ~ 77		1 ~ 7	0	9 ~ 11
C_4H_2	[a]		4 ~ 9	0	[a]
C_2H_6 feed					
CH_4	0		18 ~ 23		
C_2H_2	0		26 ~ 61		
C_2H_4	100		15 ~ 53		
C_4H_2	[a]		1 ~ 6		

[a] Not observed.

a larger scaled-up reactor (*21*). Other hydrocarbons (i.e., butane) can be selectively converted to desirable products (i.e., ethylene) in similar reactions (*22*). The use of diluent and reactive gases such as O_2 leads to the formation of substituted hydrocarbons such as HCHO and CH_3OH (*16*, *22*).

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